

**DIRECT CONVERSION OF PLUTONIUM-CONTAINING MATERIALS TO  
BOROSILICATE GLASS FOR STORAGE OR DISPOSAL**

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# DIRECT CONVERSION OF PLUTONIUM-CONTAINING MATERIALS TO BOROSILICATE GLASS FOR STORAGE OR DISPOSAL

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## ABSTRACT

A new process, the Glass Material Oxidation and Dissolution System (GMODS), has been invented for the direct conversion of plutonium metal, scrap, and residue into borosilicate glass. The glass should be acceptable for either the long-term storage or disposition of plutonium. Conversion of plutonium from complex chemical mixtures and variable geometries into homogeneous glass (1) simplifies safeguards and security; (2) creates a stable chemical form that meets health, safety, and environmental concerns; (3) provides an easy storage form; (4) may lower storage costs; and (5) allows for future disposition options.

In the GMODS process, mixtures of metals, ceramics, organics, and amorphous solids containing plutonium are fed directly into a glass melter where they are directly converted to glass. Conventional glass melters can accept materials only in oxide form; thus, it is its ability to accept materials in multiple chemical forms that makes GMODS a unique glass making process. Initial proof-of-principle experiments have converted cerium (plutonium surrogate), uranium, stainless steel, aluminum, and other materials to glass. Significant technical uncertainties remain because of the early nature of process development.

## INTRODUCTION

The end of the cold war has led to a stop in the production of nuclear weapons and a beginning of the process of disassembly of them. The latter development has resulted in an excess of plutonium that must be stored and ultimately disposed. In the near-term, there is a new requirement to store this plutonium. In the longer term, there are three disposition options:

- *Store plutonium.* Plutonium is expensive to make, and the future is uncertain in terms of national security needs and energy requirements. It can be stored in a stockpile for contingencies.
- *Burn plutonium.* Plutonium can be burned as a fuel in nuclear power plants.
- *Dispose of it as waste.*

The preferred disposition option will depend upon multiple factors: (1) national security [NS]; (2) economics; and (3) health, environment, and safety [HES]. NS considerations include any future need for the plutonium for the manufacture of weapons, disarmament agreements, strategies to control nuclear weapons nonproliferation, and strategies to prevent the theft. Recent studies (1) have examined many options. Regardless of the option or options selected, it will take time to implement any solution; hence, storage for decades will be required.

However, there are major near-term HES and NS issues. There are serious HES concerns at weapons production plants (2). Theft and recovery of plutonium have occurred in Europe. These near-term problems are primarily associated with plutonium residues and scrap rather than with plutonium weapons parts or plutonium metal in storage. Residue and scrap result from the production of nuclear weapons, research and development activities, and special applications of plutonium. There are several reasons why scrap and residue present major problems:

- The chemical compositions are highly variable. This makes treatment for storage, reuse, or disposition expensive and difficult.

- Many of the materials are in chemical forms that slowly generate gases or corrode the containers in which they are stored.
- The quantities of materials are large. The plutonium concentrations in these categories vary from a fraction of a percent to over 50%. Scrap and residue are only a small fraction of the world's plutonium, but this plutonium is mixed in with other materials so that the total volume and weight of the scrap and residue exceeds the rest of the plutonium inventory.
- Safeguards and security are difficult because it is difficult to measure the quantities of plutonium mixed with other materials in a wide variety of geometries.
- Scrap and residue exist at many more sites than do weapons components.

These factors indicate a need for new technologies to convert scrap and residue into plutonium forms that (1) ensure safe, long-term storage; (2) allow for easy safeguards and security; (3) provide for ultimate disposition; and (4) are economical. One option is described in this paper.

## NEW APPROACH TO PLUTONIUM STORAGE AND DISPOSITION

Glasses have been developed that incorporate plutonium into the glass (3). Simultaneously, the invention of GMODS (4,5) has created a process for the direct conversion of scrap and residue into glass. Earlier glassmaking processes required that plutonium feed material first be a relatively pure oxide-like material before its conversion to glass. The combination of plutonium glass forms and a process to manufacture the glass directly from scrap and residue create new options for plutonium management.

Experimental work indicates that up to 10 wt. % plutonium can be added to specific

borosilicate glasses to create a high-quality plutonium glass storage form. Such glasses would meet the requirements for a storage form that is critically safe, is in non-aerosol form, and is chemically inert [CRITICALITY, Aerosol, CHEMICAL Inert Plutonium (CRACHIP) glass]. CRACHIP refers to a set of characteristics for an ideal plutonium storage form. A CRACHIP glass eliminates most HES concerns. Simultaneously, CRACHIP glass allows the following options:

- Storage of plutonium for decades or centuries.
- Conversion of plutonium to an acceptable waste form by addition of CRACHIP glass directly to a HLW glass melter to produce a HLW glass.
- Recovery of plutonium for reuse. This would require some processing.

Four issues are discussed herein: CRACHIP glass (the product), GMODS (the process), status of technical developments, and storage of the CRACHIP glass.

## THE PRODUCT: CRACHIP

CRACHIP is a set of requirements (6) for an ideal plutonium chemical form for transport and storage that minimizes HES risks. The concept of CRACHIP is decades old. Until the end of the cold war, there was no need to store large quantities of plutonium and, hence, no incentive to deploy CRACHIP. There are several CRACHIP storage forms in addition to glass.

If plutonium is to be converted to a CRACHIP form, the choice of form must address the three primary HES hazards:

- *Inhalation.* Plutonium is highly toxic if inhaled. The characteristics of the human throat and lung are such that only small particles are capable of reaching the lung and depositing in it. Therefore, to avoid inhalation hazards, plutonium must not be allowed to form small particulates.

- *Ingestion.* Plutonium is somewhat toxic if it is ingested in water or food.
- *Criticality.* If a critical mass of plutonium is formed, a nuclear chain reaction will be initiated, thus resulting in the generation of radiation and heat until the mass is dispersed or otherwise rendered subcritical. Fatal doses of the initial radiation may occur within a few meters of the accident.

These hazards are interconnected. A major concern with plutonium in water is that the water may evaporate creating plutonium aerosols. Similarly, a major concern of nuclear criticality is that such events create plutonium aerosols and damage equipment; and thus, such events may allow a release of plutonium to workers, the public, and the environment beyond the immediate location of the accident.

To minimize these HES hazards by choice of chemical form, three sets of requirements must be met:

- *Mechanical.* A monolithic form is required that is not easily converted to aerosols upon handling or in an accident.
- *Chemical.* The form must be chemically inert and exhibit low leachability in water. Chemical reactions may generate aerosols and thus must be avoided.
- *Nuclear.* The form must contain neutron poisons sufficient such that nuclear criticality can not occur with any quantity or configuration of materials. Neutron poisons are such materials as boron and gadolinium (a rare earth element).

If the CRACHIP product is to be stored in sealed packages, there is a fourth requirement, which is to minimize helium release from the solid to avoid package pressurization. Helium is generated by the radioactive decay of plutonium. This fourth requirement is achieved for CRACHIP forms that have been proposed.

The requirements for CRACHIP are similar to those required for storage or disposal of high-level-waste (HLW) glasses. Radioactive wastes become less hazardous with time; hence, the basic concept in waste management is to isolate (store) radioactive wastes until they are non-hazardous. The criteria for selection of a good waste form are very similar to those required for CRACHIP. Glass has been chosen worldwide as the preferred HLW storage and transport form because several of its properties: (1) acceptance of impure feeds, (2) ease of manufacture, (3) low solubility in water, (4) inert chemically, (5) acceptable mechanical integrity, (6) ability to handle high heat loads from decay heat, and (7) avoidance of nuclear criticality by use of neutron poisons. The similar requirements and experience from waste management provides the basis for CRACHIP glass.

Glass has one major advantage over other CRACHIP forms: It can accept most elements in oxide form within its structure. This minimizes the need to purify plutonium scrap and residue if they are to be converted to a CRACHIP form.

The use of a monolithic CRACHIP glass simplifies safeguards and security.

- *Homogeneous, monolithic glass cylinders.* Homogeneous materials with fixed geometries are simpler to nondestructively assay than are complex mixtures of materials with changing geometries.
- *Tagging systems.* With CRACHIP forms, platinum or other microspheres can be incorporated into the solid matrix in a random manner. Such microspheres allow X-ray determination of their locations and provide an absolute assurance that the plutonium glass has not been tampered with in any way.

Table 1 shows the specific chemical composition of one plutonium borosilicate glass developed by Ramsey (3) and designed for relatively pure plutonium oxide feeds.

**Table 1. Example CRACHIP plutonium glass composition**

Compound	Mole %	Weight %
SiO <sub>2</sub>	49.4	23.8
B <sub>2</sub> O <sub>3</sub>	5.4	3.0
BaO	2.8	3.5
Al <sub>2</sub> O <sub>3</sub>	18.0	14.8
La <sub>2</sub> O <sub>3</sub>	5.8	15.2
Nd <sub>2</sub> O <sub>3</sub>	6.7	18.1
CeO <sub>2</sub>	2.9	4.0
PuO <sub>2</sub>	3.9	8.5
PbO	5.1	9.1

## THE PROCESS: GMODS

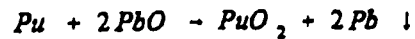
GMODS converts plutonium and the other elements within the scrap and residue directly to borosilicate glass. Existing glass making processes can only convert oxide-like material to glass. Historically, complex processes were required to convert metals, organics, and other materials to oxide form before conversion to glass.

GMODS is a batch glass process (Figure 1) during which sequential processes convert feeds to glass. The initial condition for the process is a melter filled with an oxidation-dissolution (lead borate) glass. The lead borate glass has a composition of two or more moles of PbO per mole of B<sub>2</sub>O<sub>3</sub>. The PbO is a component of the glass and a sacrificial oxide. The process consists of the following steps:

- *Addition of feed material to the molten dissolution glass.* Ceramic (plutonium oxide, etc.) and the amorphous components in the feed dissolve into the glass. Metals and organics do not dissolve into conventional molten glasses;

however, this GMODS dissolution glass has special properties. The inclusion of a sacrificial oxide in the molten glass provides a method to oxidize in situ (a) metals to metal oxides and (b) organics to carbon oxide gas and steam. When plutonium or other metal is fed to the melter, it is converted to a metal oxide. These metal oxides dissolve into the glass; carbon oxides (in gaseous form) and steam exit the melter.

The sacrificial oxide, PbO, which is a component in some glasses, reacts with metals and organics in glass to yield oxides and metallic lead (Pb):



The reaction product, molten lead, separates from the glass and sinks to the bottom of the melter to form a separate layer. Any plutonium metal that sinks through the glass without fully reacting with the glass (1) enters the molten lead, (2) dissolves into the lead, (3) is oxidized at the interface of the lead metal and glass, and (4) is extracted back into the glass. The lead at the bottom of the melter forms a liquid with a high density such that various feeds—including plutonium residues—float at the lead-glass interface while reacting with the PbO and dissolving into the glass.

The properties of lead-borate glass allow rapid oxidation and dissolution of metal, ceramic, organic, and amorphous solids into glass. The PbO in this system is a powerful oxidant. Some metals will,

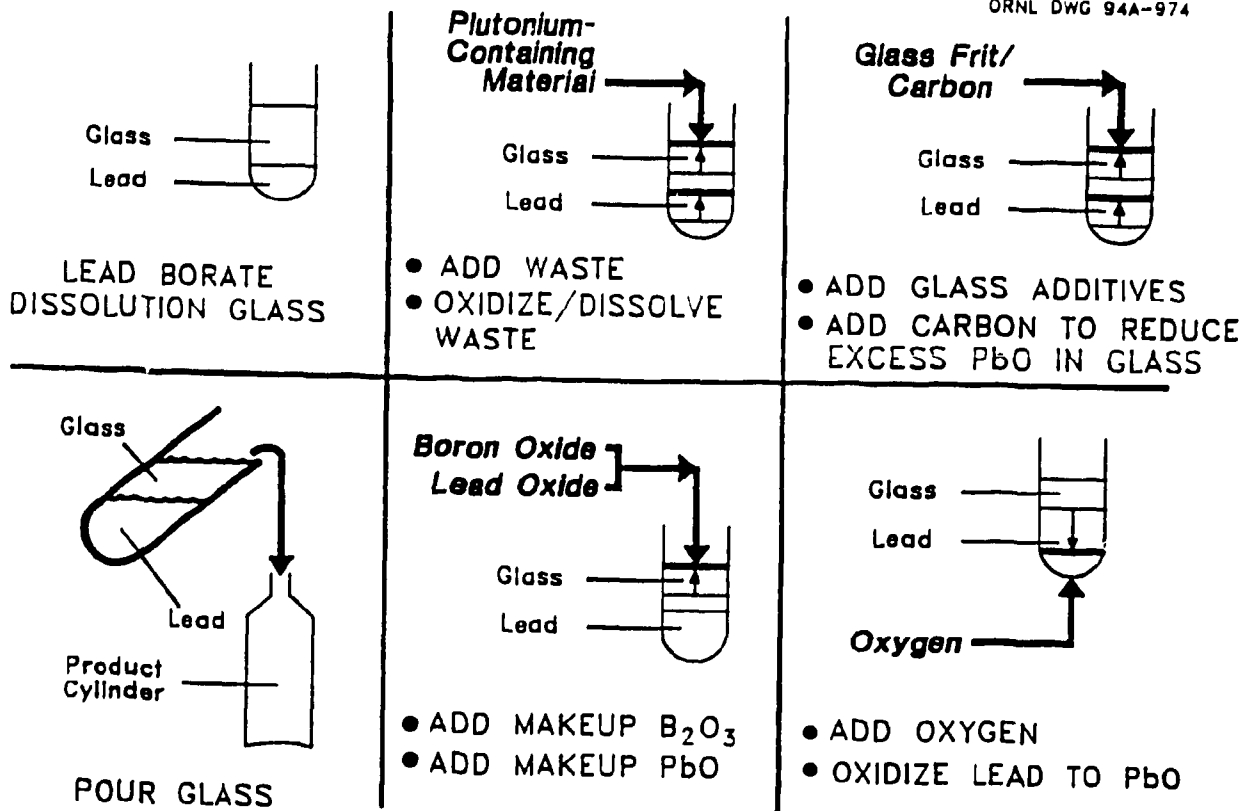
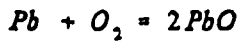


Figure 1. GMODS batch processing of plutonium-containing material to borosilicate glass.

however, form protective oxide coatings that slow chemical reactions. Boron oxide is a dissolution agent for metal oxides and rapidly solubilizes these metal oxides. It is the combination of both the PbO and  $B_2O_3$  that makes GMODS feasible.

- *Addition of additives [silicon oxide ( $SiO_2$ ) etc.] to improve the glass quality.* Optimum glasses for rapid oxidation-dissolution of materials are different in composition from glasses for long-term durability; thus, glass additives that create a more durable glass are introduced after feed oxidation-dissolution takes place.
- *Addition of carbon to remove excess PbO.* The carbon reduces the PbO to lead metal while producing gaseous carbon oxide. Excess lead oxide is removed from the dissolution glass for multiple reasons: (1) more durable glass, (2) reduction of the volume of the glass, and (3) avoidance of the costs to provide added sacrificial PbO. The final glass is chemically nonhazardous.
- *Pouring from furnace followed by solidification.*

- Addition of  $B_2O_3$  and  $PbO$ , as needed, to the melter for processing the next batch of materials.
- Reoxidation of the lead at the bottom of the melter to  $PbO$  by the addition of oxygen. This oxidation creates the new dissolution glass for the next batch of feed to be processed. Lead is an oxygen carrier that does not leave the system. The oxidation reaction is



GMODS is designed also to convert chloride-containing plutonium residues to glass and create a separate nonradioactive sodium chloride waste stream. Halogens such as chloride make poor-quality storage forms; hence, they must be separated from other components in plutonium residues. The analogy used in waste management that good storage forms for radioactive materials can be found at any ocean beach. Materials that make beach sand (silica, titanates, etc.) make good storage forms. Materials that dissolve in sea water (chlorides, etc.) make poor storage forms.

The separation process for chlorides is shown in Figure 2. In the dissolution glass chlorides in the feed form lead chloride ( $PbCl_2$ ), which is volatile at glass melter temperatures and which exits to the aqueous sodium hydroxide scrubber. In the scrubber, the  $PbCl_2$  reacts with the  $NaOH$  to yield insoluble lead hydroxide [ $Pb(OH)_2$ ] and soluble sodium chloride salt. The insoluble  $Pb(OH)_2$  is recycled back to the melter while the aqueous salt stream is cleaned and discharged as a chemical waste.

The primary GMODS equipment is an induction-heated, cold-wall melter. A cold-wall melter is required because of the corrosive characteristics of the initial dissolution glass. Cold-wall melters have cooling jackets in the wall to produce a "skull" of solidified material that protects the wall from the melter contents. Cold-

wall melters are used to melt high-temperature materials (titanium and superalloys) and to produce ultrapure materials (glass for fiber optics). Russia and France are developing cold-wall melters for processing various radioactive wastes.

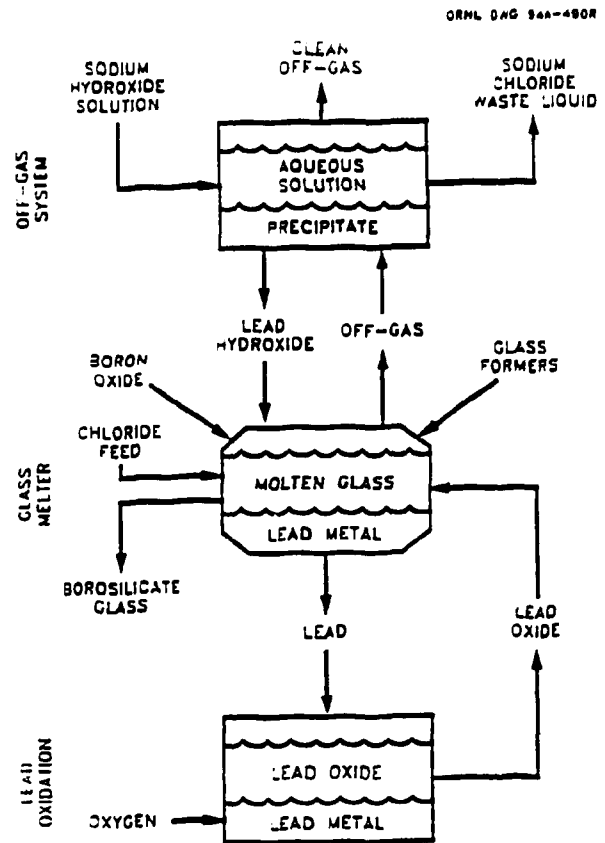


Fig. 2. GMODS processing of chloride containing feed materials.

## STATUS OF DEVELOPMENT

Laboratory quantities of plutonium glasses have been fabricated, and their properties have been measured (3) at the DOE Savannah River

Site. Experiments at ORNL (4,5) have demonstrated key steps of the GMODS process including the conversion of cerium (a plutonium surrogate), uranium, stainless steel, aluminum, Zircaloy-4, carbon, and other materials to glass. Various silicate glasses have been produced. Experiments are currently underway to demonstrate conversion of chloride streams to glass and sodium chloride salt. Significant work is required to convert the process into a standard industrial process.

### CRACHIP STORAGE

The characteristics of CRACHIP alter storage requirements. Several factors increase the storage volume required for CRACHIP glass compared to storage of plutonium metal or oxide: lower density ( $5 \text{ g/cm}^3$ ) and a maximum plutonium loading in the glass of 10% and a lower plutonium loading for some residues if the residues are directly converted to glass. Several factors decrease the storage volume required for CRACHIP compared to plutonium metal: monolithic glass cylinders that efficiently fill storage packages, limited nuclear criticality considerations, and limited HES concerns. Overall, these characteristics reduce vault space requirements.

A conceptual design of a storage block within the vault interior for CRACHIP glass is shown in Figure 3. The layout and dimensions of key components are similar to those of some spent fuel storage facilities and certain reactors (6). The CRACHIP glass is sealed in cans. The cans are stored in horizontal tubes which go between vertical shielding walls. The tube length between the shielding walls is 5 m. The CRACHIP glass can be cooled as necessary by cooling the outside of the horizontal tubes with air, helium, water, or other fluids. Weapons-grade plutonium has a decay heat load of 2.38 kW/t. Other types of plutonium have substantially higher decay heat loads. The ends of the tubes in the shield walls have shield plugs that allow manned entry to the loading face of the storage block. The shield plugs, along with appropriate locking devices, may be used as part of an internal vault within the vault. The shielding plugs may also contain

International Atomic Energy Agency safeguards seals. The vault may be loaded and unloaded manually or with stacker/retrieval devices.

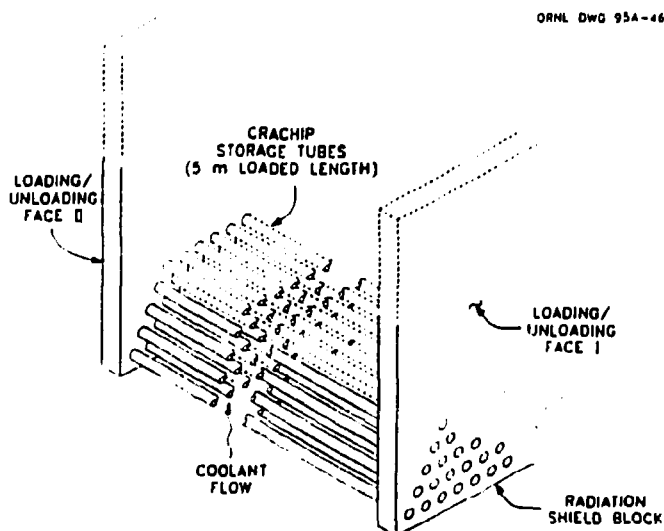


Fig. 3. CRACHIP storage block within plutonium storage vault.

The primary barrier to plutonium release is the CRACHIP glass, which is backed up by the can, storage tube, and vault. The option exists to backfill the individual plutonium cans with different mixtures of noble gases to tag individual packages. If any package fails, sample gas from any storage tube would indicate can failure and identify the failed can. Such systems have been used in nuclear reactors to identify failed fuel.

The length of the storage block would be about 5 m per 100 t of glass—assuming a 5-m-high storage block, 10-cm-diameter CRACHIP glass,  $5 \text{ g/cm}^3$  glass density, a triangular storage tube array, 20-cm spacing between center lines of storage tubes, and 80% of storage tube length filled with glass.



## SUMMARY

Glass technologies developed for waste management are creating the option of CRACHIP glass to address HES and NS concerns associated with the storage and disposition of plutonium. Simultaneously, the new GMODS glass process creates a method to directly convert plutonium metal, scrap, and residue to CRACHIP glass. Significant development will be required to reduce technical uncertainties and obtain optimum process parameters.

## REFERENCES

1. National Academy of Science, *Management and Disposition of Excess Weapons Plutonium*, National Academy Press, Washington D.C., 1994.
2. U. S. Department of Energy, *Plutonium Working Group Report on Environmental, Safety, and Health Vulnerabilities Associated With the Department's Plutonium Storage*, Washington D.C., November 1994.
3. W. G. Ramsey, N. E. Bibler, and T. F. Meaker, "Compositions and Durabilities of Glasses For Immobilization of Plutonium and Uranium," *Proceedings of Waste Management '95, Tucson, Arizona, March 1, 1995*.
4. C. W. Forsberg et al., *Direct Vitrification of Plutonium-Containing Materials*, ORNL-6825, Lockheed Martin Energy Systems, Inc., Oak Ridge National Laboratory, Oak Ridge, Tennessee (In Press).
5. C. W. Forsberg et. al., "Direct Conversion of Plutonium Metal, Scrap, Residue, and Transuranic Waste To Glass," *Proceedings of Waste Management '95, Tucson, Arizona, March 1, 1995*.
6. C. W. Forsberg, *What is Plutonium Stabilization and What is Safe Storage of Plutonium?*, ORNL/M-4322, Oak Ridge National Laboratory, Lockheed Martin Energy Systems, Inc., Oak Ridge, Tennessee (June 1995).
7. Atomic Energy of Canada Limited, *CANDU 600 Station Design*, Ottawa, Ontario, Canada.